LA-UR 93-207

LA-UR--93-207

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TITLE: THE NEED FOR MIXED WASTE TREATMENT OPTIONS WITHIN THE US DEPARTMENT OF ENERGY*

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SUBMITTED TO: Advanced Research Workshop on Non-Thermal Plasma Techniques for Pollution Control, Cambridge, England, September 21-25, 1992

*This work was performed at Los Alamos National Laboratory under the auspices of the United States Department of Energy under contract number W-7405-ENG-36

THE NEED FOR MIXED WASTE TREATMENT OPTIONS WITHIN THE US DEPARTMENT OF ENERGY

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Introduction

The United States Department of Energy (DOE) has generated and stored significant amounts of low-level mixed wastes consisting of radioactive materials mixed with hazardous chemical substances in various forms. The DOE is in the process of beginning a cleanup of these mixed wastes at many of its facilities. Many of these waste streams had been previously disposed of by methods acceptable at the time but with the passage of very stringent laws affecting migration of hazardous components, now the disposal areas constitute remediation sites. Disposal of low level radioactive waste potentially containing hazardous materials have also fallen under land disposal restrictions and currently no mixed waste is going to low level disposal facilities. "These wastes are now regulated under the US Environmental Protection Agency (EPA) Land Disposal Restrictions (LDR) and must be treated and disposed in compliance with applicable state and federal requirements. In general, LDR treatment requirements include elimination of organic hazardous constitutes and stabilization of inorganic hazardous constituents. Final waste forms must meet both EPA leach-testing and DOE disposal acceptance criteria."(Coleman 1992) Because of the lengthy political battle over whether DOE was subject to EPA regulations, development and implementation of solutions to the mixed waste problem have only begun in the last few years. As a result, the DOE currently does not have an adequate capability to meet these treatment objectives. Conventional methods of destroying the hazardous components have often either been difficult to implement, because of the radioactive component, or have met considerable opposition from the governmental or public sectors. Most of the opposition centers on concerns of pollution of the environment by either or both the radioactive and hazardous components. Innovative technical solutions for waste disposal that address public concerns on pollution are needed in as short a time as possible to address out-of-regulatory-compliance stored mixed wastes. These innovative waste destruction technologies need to have comparable or superior cost versus benefit, or performance as well as public acceptablity over baseline technologies.

The paper will address why the DOE is just now starting to comply with environmental laws, why there is a need to find more effective and less expensive means of cleaning up wastes, how the DOE is organizing to accomplish this cleanup, and several plasma technology development efforts in the DOE Complex that show promise of meeting these needs.

The US Department of Energy and RCRA

The relationship between the Department of Energy (DOE) and the Resource Conservation and Recovery Act of 1976 (RCRA)(Pub L. No. 94-580, 90 Stat. 2796) as amended, has been and continues to be abstruse at best. Indeed, ever since the Environmental Protection Agency promulgated regulations implementing RCRA in 1980, a battle of applicability of those regulations to DOE facilities has been in dispute. DOE used the language in RCRA itself to argue that its facilities were exempt from compliance even though RCRA stated that federal facilities are included in RCRA's comprehensive programs.(42USC 6905a, 1992; Train 1984; Sierra 1990)

Specifically, DOE cites the language in RCRA which states that none of the provisions in RCRA "shall be construed to apply (or to authorize any State, interstate, or local authority to regulate) any activity or substance which is subject to the Atomic Energy Act of 1954 (AEA) except to the extent that such application (or regulation) is not inconsistent with the requirements of such [ACT]."(42 USC 6905a)

DOE did not interpret the above AEA reference language as just a legislative affectation but rather as an explicit and substantive reaffirmation that the AEA essentially precludes the application of RCRA to DOE facilities.

DOE's involvement with environmental laws essentially began back in late 1975. In that year the Colorado Public Interest Research Group, Inc., filed suit in federal district court against EPA to compel the EPA to control the discharge of radioactive materials into navigable waters from the Rocky Flats Plant and the Fort St. Vrain Nuclear (Power) Generation Station.(Train 1976) In 1976, the Supreme Court held specifically that "'radioactive materials'" (source, by-product, and special nuclear materials) are not under the control of the EPA administrator; rather, such 'radioactive materials' come under the AEA as administered by theEnergy Research and Development Administration (ERDA) (predecessor agency of the DOE).

However, the Court did note specifically that other non-radioactive material pollutants *are* regulated by the EPA vis-a-vis the Clean Water Act (CWA), i.e., solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, and industrial wastes discharged into navigable water. It is important to recognize that the Court did not address directly, nor was it a question before the Court, of whether the EPA or ERDA controlled the discharge of industrial, chemical or incinerator wastes that were mixed in with radioactive wastes from nuclear weapons facilities. It is equally important to recognize that because the Court's ruling was narrowly tailored to only radioactive materials the Court did not preclude, and essentially left open the door for, future regulation under RCRA of non-radioactive wastes that are contained in a mixture of radioactive and non-radioactive wastes (commonly called mixed wastes).

It was not until 1980 that the EPA promulgated its first regulations under RCRA to manage the nation's hazardous wastes in an organized manner; nevertheless, the DOE maintained that RCRA did not apply to mixed wastes because, inter alai, (1) the AEA precluded regulation of DOE activities, including waste generation, storage and disposal, by the EPA or state environmental agencies,(42 USC 6927,1992) and(2) the data pertaining to those wastes is restricted from public release under the AEA. Accordingly, DOE asserted that RCRA was "inconsistent"(42 USC 2201(i)(3),1992) with the AEA and the operation of nuclear weapons facilities; hence, RCRA did not apply to DOE's nuclear facilities or its wastes.(Train 1984)

DOE's argument that its nuclear facilities and mixed wastes were not under RCRA was put to the test in a 1984 federal court case. In that year the Legal Environmental Assistance Foundation, Inc., (LEAF), Natural Resources Defense Council, Inc., and the State of Tennessee filed suit in US District Court against Donald Hodel, Secretary of the Department of Energy and the DOE itself for RCRA and CWA violations at the DOE Y-12 Plant in Oak Ridge, Tennessee.(LEAF 1984)

In this landmark ruling the US District Court held that the hazardous waste component(s) of mixed wastes from the Y-12 plant were subject to RCRA. However, the court held also that if the application of RCRA to mixed wastes was inconsistent with the AEA, then the AEA took precedence. (LEAF 1984) As to the issue that RCRA was in conflict with secret data, the court held that the DOE upon its determination should apply for a Presidential exemption from RCRA if security concerns exist for specific mixed wastes.(LEAF 1984) As a result of the court's holding, the AEA regulates the radioactive component of mixed wastes while RCRA regulates the hazardous component of mixed wastes. While on the surface it may first appear that the operation of nuclear weapons production facilities would be in conflict with RCRA only few notable inconsistencies actually arise between the two Acts.[1]

While it appears to be firmly established that DOE mixed wastes are subject to RCRA, the substantive issue at this juncture is whether by-product process materials[2] (secondary effluent streams) from a nuclear weapons production facility are a waste under RCRA or a part of a common DOE product/waste management program. Current management and mechanisms to address this issue are at present unresolved on a national scale. Secondary effluent streams from one DOE plant in a particular state are subject to RCRA and designated as a hazardous waste under RCRA while that same plant's wastes having been already shipped to another out-of-state DOE facility are designated not subject to RCRA.

The intractability of the issue of whether secondary effluent streams are under RCRA or are under AEA[3] is still being litigated even into the 1990s.(Sierra 1990) Until this issue is finally resolved either in the courts (on a case-by-case basis) or by the US Congress, continuity in the overall management of DOE's nuclear weapons legacy materials or wastes will not be achieved. Accordingly, a very limited volume of mixed wastes can either be transported to or processed/treated at other DOE facilities - thereby leaving the secondary effluents unprocessed or untreated and leaving state environmental agencies unhappy and ready to file suits against the DOE facilities within its jurisdiction.

After the 1984 decision on the applicability of RCRA to mixed wastes, the US DOE relied primarily on each DOE site to work with the local regulatory authorities as to what the interpretation of the 1984 court decision would be when applied to the site's stored and newly generated wastes. The sites were then to establish a plan for compliance with the local regulatory bodies. Technology development for compliance tended to be very site specific, addressing only waste characteristics and volume at individual sites. With the inability of the Nevada Test Site to dispose of mixed waste and the beginning of closure of facilities at several DOE Complex sites the mixed waste problem was becoming more of a national issue and less of a site specific one. An integrated approach for the entire DOE Complex was needed to expedite development of solutions and minimize cost by eliminating duplication.

With this background of few acceptable methods for mixed waste disposal and a driving need to find acceptable solutions, the DOE has embarked on a national mixed waste program to develop solutions to the waste disposal problem. A systems approach of looking at all necessary steps to convert a waste stream as it presently exists to a final form acceptable for disposal is being undertaken. Baseline technologies for each step are analyzed for acceptability and potentially better or more innovative technology candidates are compared to the baseline. Technologies that compare favorably to the baseline offer options for more effective destruction of the hazardous components, reduced or eliminated secondary hazardous waste generation, and/or offer a solution that may be more acceptable and easily permittable. This program is

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[1]Since the 1984 court holding in LEAF, the DOE has not requested nor has the President seen fit to grant a Presidential exemption of mixed wastes arising from DOE nuclear weapons production facilities.

[2]In this sense the term by-product process material means material that is generated subsequent to the production of plutonium weapons in a DOE facility. Specifically, the term is not intended to incur the "by-product material" definition in 42 U.S.C. 2014(e) "'by-product material' means any radioactive material...yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material."

[3]This issue continues to be significant to DOE because of the lack of a national cohesive plan that either defines management of secondary effluent streams as an essential part of a whole process, and;thus, secondary waste streams are not a waste under RCRA or unless it can be demonstrated that such streams are, for example, feed material for actual primary processes.

developing a close working relationship with the EPA and, where possible, the affected state regulatory agencies to improve their understanding of the DOE's needs and to help expedite the permitting process.

"The Mixed Waste Treatment Project (MWTP) has been established by DOE to coordinate and to define needed national Low Level Mixed Waste (LLMW) [4] treatment capabilities as a basis for either a prototype plant design or an existing facility modification. Existing DOE mixed waste data bases have been analyzed to identify the range of waste quantities and types and to define broad treatment categories as a starting point. Over 700 mixed waste streams were classified into categories that require similar processing steps for assignment of baseline treatment."(Ross 1992) A baseline flow sheet defining process steps from receipt through final form was constructed. From this baseline flow sheet, functional and operational requirements (F&OR) for each process train were developed. An initial set of near-term technologies was identified for each process step, and alternative near-and long term options were listed. Based on these analyses, technology gaps and improvement needs in the areas of characterization, waste handling, segregation and sorting, size reduction, decontamination, materials recycle, primary and secondary treatment for RCRA compliance, off-gas treatment, and final waste form were identified.

In support of the MWTP the DOE Office of Technology Development (EM-50) is conducting ongoing research, development, demonstration, tests and evaluation to assist the Offices of Environmental Restoration (EM-40), and Waste Management (EM-30) within the DOE Office of Environmental Restoration and Waste Management in selecting alternative treatment methods for mixed wastes.

The goals of the EM-50 program are to assist in establishing system requirements, and to enhance or improve the baseline technologies such that the chosen treatment systems can be implemented at lower costs, and at lower risk than the baseline. The major baseline technology for destruction of combustible waste is incineration. Conventional incineration technology may be able to meet regulatory requirements, although there is considerable debate as to whether substantial improvements in destruction and off-gas handling will be required to meet the new Clean Air Act (CAA). Also, incineration suffers from a very unfavorable position with the public and, when radioactive constituents become part of the potential emissions, that public position becomes hostile. The MWTP is supporting a number of plasma based technologies that may meet the goals of lower cost, more effectiveness, and better public acceptability. Plasma technologies have already begun to play important roles as potentially more effective methods for organic waste destruction in environmental remediation and waste treatment. Several plasma technologies are being planned or have been successfully tested at a contaminated spill site where trichloroethylene (TCE) is being pumped from the ground and the plasma systems destroy the TCE in air before it is released to the environment. This has significant advantages over conventional approaches such as carbon absorption which is fairly expensive, tends to degrade rapidly due to non-selective absorption, and presents a secondary waste that requires destruction. Similar technologies such as in situ corona discharge have been or will be applied to carbon tetrachloride (CCl_4) spills at other DOE sites.

Hot plasma systems are being considered for primary destruction of combustible and hazardous constituent contaminated waste. This process has the potential advantage of removing the organic hazardous components, volume reduction and encapsulation of the non-combustible components in a glass matrix. Cold plasma technologies are being tested as potentially more versatile, if not more effective secondary units, for replacement of conventional thermal treatment units. Conventional thermal treatment has the disadvantages of creating NO_x problems, greatly increasing the volume flow through the system making scrubbing and

[4] Low Level Mixed Wastes is defined as wastes containing both a radioactive and regulated hazardous component. The concentration of the radioactive component meets DOE guidelines for activity, typically < 100 nanocuries/gram of matrix material.

particulate removal more difficult, and generally not responding well to upset conditions unless substantially oversized for normal operations. Plasma systems have shown advantages such as rapidly adjusting power loads to meet large swings in pollutant concentrations, removing pollutants without increasing gas volume flow, and generally less susceptibility to corrosion due to lower temperature of operation.

Several of these plasma development activities within the DOE Complex will be discussed in detail below to illustrate how specific needs are potentially being solved by innovative approaches that offer significant advantages over conventional methods.

Plasma Technology Development: VOC Destruction for ER Sites

Incineration for very low volatile organic compound (VOC) concentrations, although the conventional approach, has three major drawbacks: combustion can be incomplete, which releases some of the hazardous materials, or creates others; it is generally inefficient because of the large enthalpy that must be added to the waste stream; and fuel must be added to supply the enthalpy, so the size of the waste stream is increased considerably, rendering effective particulate removal difficult. Although incineration is still considered a best available technology, public acceptance has drastically affected the licensing of incinerator facilities. Absorption of VOCs by activated carbon shares some similar drawbacks: regeneration does not effectively destroy the hazardous compounds or the amount of waste is increased from the mass of saturated cannisters, if storage or disposal is employed.

Non-thermal plasma methods of destroying hazardous organic wastes have been demonstrated at laboratory and pre-pilot plant scale. These methods involve the generation of highly reactive oxyradicals and their reaction with organic compounds. Cold plasmas, such as those created by electrical discharges in gases, can efficiently generate copious quantities of reactive free radicals in a gaseous waste stream from the dissociation of molecular oxygen by energetic electrons in the discharge With some water present, the primary radicals are $O(^3P)$ and OH , which can break carbon and halogen bonds, producing non-hazardous compounds (primarily CO_2, H_2O, and other manageable by-products). One of the most promising technologies for cold plasma processing is based upon the "silent electrical discharge" (SDP) that has proven to be industrially dependable for the generation of large quantities of ozone. For treating gaseous or volatilizable hazardous organic wastes, this process is projected to be economically competitive with existing treatment methods. The advantages of SDP include high throughput, superior destruction efficiency, low temperatures, and straightforward engineering. The process can be closed-loop, thereby bypassing the venting of destruction products or undestroyed waste to the environment. (Rosocha, L.A.& McCulla, W.H.,1991)

A pre-pilot-scale SDP laboratory is presently set up at the Los Alamos National Laboratory, Los Alamos, New Mexico, which has been used to demonstrate cold plasma destruction of compounds directly applicable to VOC off-gas waste streams (at gas flows of 10 liter/min, TCE concentrations of 650-1,000 ppm). Both rectangular and cylindrical geometry high-power plasma cells, which are patterned after standard high-power density ozonizer cells, have been employed and are available for this work.

Aliphatic hydrocarbons, chloro-fluoro carbons (CFCs), and TCE have been processed by these SDP systems to date (preparations are now almost complete to handle CCl_4). At concentrations of 1000 to 3000 ppm hydrocarbons and 200 ppm trichlorotrifluoroethane(CCl_3CF_3) in air, destruction of 80% to 90% or greater was observed for all constituents. carbonyl chloride ($COCl_2$) and carbonyl fluoride (COF_2) were observed when only dry air was used, but with the addition of 2% water vapor, no carbonyl halides were observed and the principal products were carbon dioxide (CO_2), carbon monoxide (CO), and presumably hydrogen chloride (HCl) and hydrogen fluoride (HF), although these were not directly observed. The destruction of TCE in an argon/oxygen/saturated water vapor mix has been quite significant. Approximately 650 ppm of TCE fed to the plasma cell at 10 liter/min has been reduced to less than 1 ppm in the effluent, with a few 10s of watts of electrical power delivered to the gas. Optimization tests are now in progress and a higher throughput cell (100's SCFH) is being finalized.

High-energy electron beams (Mathews, A.j., 1991), x rays (Bremsstrahlung), and gamma rays (Mincher, B.J., 1991) have been shown to be effective for the removal of hazardous organic contaminants in water and gases and show great potential as a generally applicable technology for the destruction of organics in other waste streams (e.g. mixed wastes). Lawrence Livermore National Laboratory (LLNL) and the Idaho National Engineering Laboratory (INEL) have jointly investigated the decomposition of chlorinated hydrocarbons using ionizing radiation. Bremsstrahlung radiation (x rays) produced by electron accelerators and gamma photons from spent reactor fuel were used as sources of ionizing radiation for these investigations.

A demonstration for the remediation of VOC-contaminated groundwater at LLNL Site 300 was completed by directly treating a vacuum-extracted air stream with an electron beam. A 2.5-MeV, 1-kW average power converted x-ray machine was used as the electron-beam irradiation source. The extracted air stream contained approximately 60 ppm of TCE and was treated at a flow rate of 270 SCFM (7560 std liter/min). At these conditions, 99.8% removal of the TCE was obtained. Taking into account an accelerator beam production efficiency of 10% and an e-beam energy deposition efficiency of 33% gives a performance figure of merit of about 77 kW-hr/kg of removed TCE. These tests demonstrate great promise for large-scale e-beam treatment. Advances in radiolytic technology can perhaps decrease this by factors of 2 to 5.

Plasma Secondary Treatment for Thermal Systems

Based upon past analysis, the Rocky Flats Plant, Golden,CO. has identified the need to explore alternatives to incineration of combustible wastes and the need to evaluate additional technologies for the treatment of hazardous organic wastes. (Rosocha, L.A. et al.,1991) The SDP process was evaluated as a post-incinerator treatment process of cutting fluids and hydrocarbon oils. Encouraging results from that evaluation lead to construction and testing of a combined, two-stage packed-bed reactor (PBR) - SDP apparatus for treating chlorocarbon-contaminated machining oils (with a focus on TrimSol)^{TM}. Major goals for this system are the determination of the process material balance (including characterization of influent composition, destruction products, and effluents) and determination of the energy input and destruction efficiency of the two-stage process. This effort is intended to provide the Rocky Flats Plant with a prototype-scale evaluation of this particular incinerator-alternative technology.

The packed-bed reactor is a thermal treatment unit, not an incinerator. It consists of a fuel atomizer and injector, an alumina-filled metal cylinder, and an electric furnace. At Los Alamos, we have extended packed-bed reactor operation into a high temperature regime (above 1200 C). The existing packed bed has demonstrated the conversion of hydrocarbon-chlorocarbon liquid mixes into simpler chemical compounds by thermal combustion. The combustible liquids (i.e., cutting fluid simulants) are injected into the reactor while keeping the fuel-oxidizer ratio well below the lower combustion limit. By keeping the fuel lean, and by partially controlling the combustion reactions with the external electric furnace, no flame is produced.

Silent Discharge Plasma technology has been demonstrated at Los Alamos and elsewhere for the fine destruction (~ppm) of gaseous hazardous organic wastes, or air toxics (e.g., 1000 ppm TCE, to 100s ppb). Coupled with the packed bed reactor, a viable alternative to incineration and other methods of treating combustible liquids containing hazardous organic wastes is available. This technique allows efficient breaking of carbon and halogen bonds, producing non-hazardous compounds (primarily CO_2, H_2O, and other manageable by-products).

The two-stage process is projected to be economically competitive with existing treatment methods and offers performance advantages as well, such as closed-loop cycles, short treatment residence times, and superior destruction efficiency. Field-treatment apparatus can generally be simple and compact. In contrast to fueled incineration or adapted aqueous-based treatment systems, the volume of waste is not significantly increased.

Conclusion

Cold plasma systems offer potential advantages to the DOE for the cleanup of hazardous and mixed wastes. Many appear to offer equal or superior economics over conventional approaches and some have better performance in removing hazardous constituents than the baseline technology. Since much of the DOE's waste requires some form of volume reduction with organic contaminant destruction, plasma processes may avoid the stigma of incineration and find greater public acceptance. This greater public acceptance needs to be proven but, considering that incinerator permits require many years of preparation, review, and public comment with no guarantee that a permit will be issued, a more permittable process is certainly in the best interest of the DOE in accomplishing its cleanup mission. Plasma technology has already begun to make some significant inroads in waste destruction and pollution abatement, particularly within the Department of Energy Complex. But it still does not enjoy the kind of confidence that conventional thermal technologies enjoy. We can hope that as the plasma technology matures and we are able to show not only significant technical and economic advantages but also reliability that plasmas will become the methods of choice for waste destruction and pollution control.

Coleman, J. (1992)," Mixed Waste Treatment Project--Scope a.id Status," *Waste MAnagement 92,* Tucson, AZ, Technology and Programs for Radioactive Waste Management and Environmental Restoration, March,1992,PA 1123

LEAF, 586 F. Supp. at 1165. (1984)

Pub. L. No. 94-580, 90 Stat. 2796 (codified as amended at 42 U.S.C.A 6901-6991i (West 1990 & Supp. 1992) (in 1980, the EPA began its rulemaking implementating RCRA which, *inter alai,* established an extensive "cradle to grave" program for hazardous wastes, involving regulations on hazardous waste generation, treatment, storage, disposal, and transportation).

Rosocha, L.A. and McCulla, W.H., "Non-Equilibrium Plasma Combustion of Hazardous Organic Compounds Using Silent Discharge Plasmas", *44th Annual Gaseous Electronics Conference,* Albuquerque, NM, October 1991

Rosocha, L.A., McCulla, W.H., Anderson, G.K., Coogan, J.J., Kang, M., Tennant, R.A., and Wantuck, P.J., "Nonthermal Plasma Alternatives to the Incineration of Hazardous Organic Wastes", *Proceedings of the 11th International Incineration Conference,* Albuquerque, NM, 1991, PA 179-185

Ross, W.A., "Location, Volumes, and Characterization of DOE's Mixed Low-Level Wastes",*Waste MAnagement 92,* Tucson, AZ, Technology and Programs for Radioactive Waste Management and Environmental Restoration, March,1992, PA 1127

Sierra Club v. United States Department of Energy and Rockwell International Corp., 734 F. Supp. 946 (D. Colo. 1990) (where the court held, *inter alai,* that incinerator ash was a hazardous waste under RCRA because the plutonium in the materials incinerated were not available for immediate reuse, and; thus qualify for a recycling exemption under RCRA; Sierra Club v. United States Department of Energy, 770 F. Supp. 578 (D. Colo. 1991) (where the court held, *inter alai,* that DOE must obtain a RCRA permit for illegally stored mixed wastes).

Train v. Colorado Public Interest Research Group, Inc., 426 U.S. 1 (1976).

Train, 426 U.S. 1; Legal Environmental Assistance Foundation (LEAF) v. Hodel 586 F. Supp. 1163 (E.D. Tenn., 1984).

42 U.S.C. 2201(i)(3). (1992)

42 U.S.C. 6905(a). (1992)

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